#### CIA-RDP86-00513R001755810009-5 "APPROVED FOR RELEASE: 07/16/2001

5 (3) AUTHORS: Tinyakova, Ye. I., Dolgoplosk, B. A., SOV/79-29-7-61/83 Zelenina, T. P.

TITLE:

Redox Systems for the Initiation of Radical Processes (Okislitel'no-vosstanovitel'nyye sistemy dlya initsiirovaniya radikal'nykh protsessov). X. On the Mechanism of the Effect of Redox Systems With the Participation of SO2 (X. O mekhanizme deystviya ckislitel'no-vosstanovitel'nykh sistem s uchastiyem

so,)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2377 - 2381

(USSR)

ABSTRACT:

Sulfur dioxide, by reason of its duality, may be used in redox systems in combination with both oxidizing agents (peroxides, hydroperoxides) and reducing agents (mercaptans, H2S, and di-

enols). As was shown by the authors (Refs 1,2) these systems may be used to induce radical reactions in hydrocarbon media (Refs 1,2). In the present paper experimental data is given which makes an interpretation of the mechanism of the effect of the above systems possible. The reaction of isopropylbenzene-hydroperoxide with SO2 is extremely fast in hydrocarbon

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APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

Redox Systems for the Initiation of Radical Processes. X. On the Mechanism of the Effect of Redox Systems With the Participation of SO<sub>2</sub>

507/79-29-7-61/83

solutions and causes a rapid gel formation in rubber solutions. This reaction is accompanied by the formation of polysulfone if styrene is used as a solvent. Nitrogen monoxide prevents this process. Analysis of the reaction products obtained with and without NO proved the reaction to proceed via the radicals (SO<sub>3</sub>H), which react with the monomer to give sulfonic acid. It was shown previously (Ref 2) that the reaction of trichlorothiophenol with SO<sub>2</sub> produces a vulcanization of rubber at low temperatures. Thus, this reaction leads to the formation of unsaturated polymers. Its mechanism is that of a chain reaction and the reaction proceeds accordingly, and is accompanied by the addition of trichlorothiophenol and SO<sub>2</sub> to the unsaturated polymer chain. NO prevents this process. There are 3 tables and 7 references, 4 of which are Soviet.

Card 2/3

Redox Systems for the Initiation of Radical SOV/79-29-7-61/83 Processes. X. On the Mechanism of the Effect of

Redox Systems With the Participation of SO2

ASSOCIATION: İnstitut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR

(Institute of High-Molecular Compounds of the Academy of

Sciences, USSR)

SUBMITTED: June 16, 1958

Card 3/3

5.3831	67919
≶ <del>(3)</del> AUTHORS:	SOV/20-129-5-29/64 Tinyakova, Ye. I., Dolgoplosk, B. A., Corresponding Member, AS USSR, Zhuravleva, T. G., Kovalevskaya, R. N., Kuren'gina, T. N.
TITLE:	Polymerization of Dienes and Olefins Under the Action of Cobalt Oxides and Diethyl Aluminum Halides, and a Study of the Structure of Polymers
PERIODICAL:	Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 5, pp 1068 - 1070 (USSR)
ABSTRACT :	The authors supply data concerning the polymerization of dienes: butadiene, isoprene, pentadiene-1-3, and 2-3-di-1 methyl butadiene-1-3, as well as olefins: α-butene, styrene and α-methyl styrene in the presence of cobalt oxides (Co <sub>2</sub> O <sub>3</sub> -Co <sub>3</sub> O <sub>4</sub> , Ref 6), and diethyl aluminum chloride or di-
Card 1/4	ethyl aluminum bromide. The catalyst contained either 71-73% or 6.7% of Co. The latter content refers to cobalt oxide on aluminosilicate. Polymerization was carried out between O and 40° in different ratios between cobalt oxide and diethyl aluminum halide (concentration 0.5-2.5 of weight per

APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

Polymerization of Dienes and Olefins Under the SOV/20-129-5-29/64 the Structure of Polymers

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cent referred to the monomer). Oxygen and humidity were kept off. In the polymers produced the content of 1-2-, 3-4- and 1-4-cis- and trans-members was determined by IRspectroscopic measurement (spectra taken by N. V. Mikhaylova). The unsaturation was determined on the basis of the reaction with iodine chloride (Ref 7). The vitrification temperature was determined according to A. I. Marey (Ref 8). Table 1 gives the results along with the molecular weight. Under mentioned conditions butadiene is rapidly polymerized already at 0°. Cobalt oxide on aluminosilicate retards polymerization to some extent. The polymers obtained exhibit a degree of unsaturation which is 97.5-99% of theory. This points to the absence of secondary reactions with the double bonds of the polymer. Butadiene polymers have a fairly regular microstructure. On cobalt oxide without carrier the amount of the 1-2-members was 5-8%, the total amount of the 1-4-members was 95-92%, with the most part being in the 1-4-cis-position. By the use of cobalt oxide on

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APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

Polymerization of Dienes and Olefins Under the SOV/20-129-5-29/64 Action of Cobalt Oxides and Diethyl Aluminum Halides, and a Study of the Structure of Polymers

aluminosilicate, the amount of the 1-2-members in the chain rises. Due to the high content of 1-4-members this polybutadiene has a low vitrification temperature (down to -115°). Isoprene is polymerized more slowly and at higher temperatures (at about 40°) as compared to butadiene. Here too, the process runs more slowly with the use of aluminosilicate as carrier. It may be observed from table 1 that both the microstructure of polyisoprene and the vitrification temperature are not changed appreciably by the concentration of the aluminum-organic compound nor by the ratio between cobalt oxide and aluminum diethyl halide. Fairly large amounts (17-18%) of isopropenyl side-groups increase the vitrification temperature of the polymer considerably. The total content of 1-4-members is about 80%; their major part is in the trans-position. A further strong retardation of polymerization takes place in the transition to higher dienes.  $\alpha$ butene is not quickly polymerized at room temperature and does form no more than a caoutchouc-like substance. Neither styrene nor  $\alpha$ -methyl styrene are polymerized by the procedure de-

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Polymerization of Dienes and Olefins Under the SOV/20-129-5-29/64 Action of Cobalt Oxides and Diethyl Aluminum Halides, and a Study of the Structure of Polymers

scribed. Finally the authors state that no gaseous hydrocarbon products are formed in the interaction between cobalt oxides and an aluminum-organic compound at 0 to 80°. There are 1 table and 9 references, 5 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-molecular Compounds of the Academy of Sciences, USSR)

SUBMITTED: September 5, 1959

Card 4/4

APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

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5 (3) AUTHORS:

68164

Tinyakova, Ye. I., Dolgoplosk, B. A., SCV/20-129-6-30/69

Corresponding Member, AS USSR,

Kovalevskaya, R. N., Zhuravleva, T. G.

TITLE:

Polymerization and Copolymerization of Dienes and Olefines on

a Chromium Oxide Catalyst

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 6, pp 1306 - 1308

(USSR)

ABSTRACT:

The authors (Tinyakova and Dolgoplosk) proved in a previous paper (Ref 1) that polymerization of butadiene and isoprene on a chromium oxide catalyst yields crystalline polymers containing only 1 - 4 links in trans position in the chain. Polymers of pentadiene-1 - 3. of α-butene, as well as a copolymer of dienes and olefines which are formed by polymerization on the above catalyst are described in the paper under review. Polymerization and copolymerization were carried out under conditions equal to those of the previous experiments (Ref!). Contrary to butadiene-7 and isoprene, //pentadiene-1 - 3 yields an amorphous

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polymer, soluble in benzene, specific weight = 0.89. Its vitrification temperature is  $-60^{\circ}$ , its unsaturation 97% of the

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Polymerization and Copolymerization of Dienes and Olefines on a Chromium Oxide Catalyst

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theoretical value. Fragments connected in position 3-4 are missing in its chain. Most of the 1-4 links are deposited in a trans position. On a chromium oxide catalyst, a-butene yields a crystalline fibrous polymer partially soluble in hot toluene and boiling diethyl ether (about 30%); its specific weight is 0.96. Figure 1 shows the dispersion curves of X-rays on poly-αbutene between 20 and 1500. A distinct maximum proves the crystalline structure of the polymer. A. N. Andreyeva carried out the radioscopic investigation by means of the X-ray apparatus of type URS-50. The crystals melt at about 140°. Modification I exists up to 40°, modification II between 60 and 140°. Both modifications exist at about 50°. In the case of natural rubber and gutta-percha, the vitrification temperature of polymers with cis and trans configurations of the links is practically equal (-71°). Vitrification at -110° was to be expected in the case of transpolybutadiene. Table 1 shows that the polymer loses its crystallizing power due to copolymerization of butadiene or isoprene with other compounds. The polymer becomes highly elastic. These transformations are due to the destruction of the trans-1-4 structure. Amorphous elastic products are formed by copolymeriza-

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Polymerization and Copolymerization of Dienes and Olefines on a Chromium Oxide Catalyst

68164 SOV/20-129-6-30/69

tion of mixtures of butadiene with isoprene and pentadiene -1 - 3 as well as of isoprene with ethylene. Their vitrification temperature ranges between the vitrification temperatures of the polymers from corresponding monomers (Table 1). In all cases, a monomer mixture polymerizes more slowly than each individual monomer by itself (Fig 2). All butadiene and isoprene links in the chain are only in trans-! - 4 position as was proved by infrared spectroscopy (photographs by K. V. Nel'son) in the elastic amorphous polymer from butadiene and isoprene (equimolar). The polymer contains 55% of butadiene links as was computed from the unsaturation values (Table 1). The vitrification temperature of the amorphous isoprene ethylene transpolymer is lower than that of natural rubber In the case of butadiene, a highly elastic state could be attained only by copolymerization with isoprene and pentadiene-1 - 3. There are 2 figures, 1 table, and 5 references, 3 of which are Soviet.

ASSOCIATION:

Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-molecular Compounds of the Academy of Sciences, USSR)

SUBMITTED:

September 5, 1959

Card 3/3

TINYAKOVA, Ye. I., Doc Chem Sci (diss) -- "The initiation of chain radical processes under the influence of oxidation-reduction systems". Leningrad, 1960. 21 pp (Acad Sci USSR, Inst of High-Molecular Compounds), 250 copies (KL, No 11, 1960, 129)

TEXTS IN THE THE PROPERTY OF T

Present-day problems of synthetic rubber; synthesis of rubber for general purposes. Khim.prom. no.10:55-67 0 '61; (MIRA 15:2)

(Rubber, Synthetic)

S/064/61/000/0:1/002/007 B101/B147

AUTHORS:

Dolgoplosk, B. A., Tinyakova, Ye. I.

TITLE:

The present state of the problem of rubber synthesis

(Synthesis of special-purpose rubbers)

PERIODICAL: Khimicheskaya promyshlennosti, no. 11, 1961, 52 - 60

TEXT: This is a survey on literature data concerning the synthesis of rubbers resistant to frost, gasoline, heat, heat and gasoline, and of polysiloxane rubbers. There are 4 tables and 78 references: 26 Soviet and 52 non-Soviet. The four most recent references to English-language publications read as follows: R. H. Buddulph, W. R. Longworth, P. H. Plesh, Polymer, 1, 521 (1960); H. Kavai, R. S. Stein, J. Appl. Pol. Sci., 4, 439 (1960); Chem. Eng. News, 38, 107 (1960); C. B. Pierce, Ind. Eng. Chem., 52, 783 (1960).

Card 1/1

DOLGOPLOSK, B.A.; TINYAKOVA, Ya.I.

Present state of knowledge of rubber synthesis (synthesis of rubbers for special uses). Khim.prom. no.ll:794-802 N '61.

(Rubber, Synthetic)

(MIRA 15:1)

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AUTHORS:

Reykh, V. N., Dolgoplosk, B. A., Tinyakova, Ye. I., Kalaus,

A Ye.

TITLE:

Properties of carboxyl-containing rubbers

PERIODICAL:

Referativnyy zhurnal. Khimiya, no 15, 1961. 600, abstract 15[1354 (Sb. "Vulkanizatsiya rezin izdeliy". Yaroslavl',

1960, 43 - 55)

TEXT: Results of preliminary tests of butadiene styrene (K-1-30(SK-1-30) divinyl and isoprene rubbers with additions of methacrylic acid are given. Rubbers from SK-1-30 surpassed the rubbers from CK(-30 (SKS-30A) with respect to stability to pure-gum mixtures, thermal stability, resistance to thermal aging, widening of cuts, wear, and with respect to elasticity. Carboxyl-containing isoprene rubber shows the least heat release on repeated deformation. [Abstracter's note: Complete translation.]

Card 1/1

DOLGOPLOSK, B.A.; TINYAKOVA, Ye.I.

Mechanism of diene polymerization and the structure of the polymer chain. Dokl. AN SSSR 146 no.2:362-365 S '62. (MIRA 15:9)

1. Institut khimicheskoy fiziki AN SSSR. 2. Chlen-korrespondent AN SSSR (for Dolgoplosk).
(Butadiene) (Polymerization)

DOLGOPLOSK, B.A.; TINYAKOVA, Ye.I.

Mechanism underlying the action of complex catalysts in the process of polymerization. Dokl. AN SSSR 146 no.4:856-859 0 '62. (MIRA 15:11)

1. Institut khimicheskoy fiziki AN SSSR. 2. Chlenkorrespondent AN SSSR (for Dolgoplosk). (Polymerization) (Catalysis)

KOVALEVSKAYA, R.N.; TINYAKOVA, Ye.I.; DOLGOPLOSK, B.A.

Study of heterogeneous catalyst systems based on cobalt oxides and salts, and organoaluminum compounds. Vysokom. soed. 4 no.9:1338-1344 S '62. (MIRA 15:11)

1. Institut vysokomolekulyarnykh soyedineniy AN SSSR. (Polymerization) (Cobalt catalysts) (Aluminum organic compounds)

APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

TINYAKOVA, Ye.I.; ZHURAVLEVA, T.G.; KUREN GINA, T.N.; KIRIKOVA, N.S.; DOLGOPLOSK, B.A.

**。 1980年 - 19** 

Cation activity of components of complex catalysts. Dokl.AN SSSR 144 no.3:592-595 My 162. (MIRA 15:5)

1. Institut vysokomolekulyarnykh soyedineniy AN SSSR. 2. Chlen-korrespondent AN SSSR (for Dolgoplosk).

(Catalysts) (Polymerization) (Cations)

APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

S/190/62/004/009/006/014 B101/B144

AUTHORS:

Kovalevskaya, R. N., Tinyakova, Ye. I., Dolgoplosk, B. A.

TIPLE:

A study of heterogeneous catalytic systems on the basis of cobalt oxides or salts and organoaluminum compounds

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 9, 1962, 1338-1344

TEXT: An examination of the polymerization of butadiene or isoprene by catalytic systems consisting, on the one hand, of  $CoCl_2$ ,  $CoBr_2$ ,  $CoSO_4$ ,  $CoO_5$ , on the other hand, of  $Al(C_2H_5)_2Cl$  or  $Al(C_2H_5)_3$  in benzene showed the following results: (1) The reaction takes place at room temperature. Polybutadiene contains up to 90%, and polyisoprene up to 65 - 70% cis-1,4 bonds. (2) Redox reactions do not occur between  $(C_2H_5)_2AlCl$  on the one hand and  $CoCl_2$ ,  $CoO_5$ ,  $CoO_5$ 0 on the other hand. The amount of  $(C_2H_5)_2AlCl$  in the mixture does not change, and gaseous compounds do not form between 20 and 80°C. The complex which initiates the catalysis has the composition  $CoCl_2AlR_2Hal$  or  $CoO^5AlR_2Hal$ . (3) The system  $(C_2H_5)_3Al$  + CoO is inactive.

S/190/62/004/009/006/014

A study of heterogeneous catalytic... B101/B144

The system (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al + CoCl<sub>2</sub> is active only in so far as diethyl aluminum chloride is formed. Without monomers, the reaction followed the equation 2A1(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> + CoCl<sub>2</sub> → 2A1(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl + Co + mC<sub>2</sub>H<sub>6</sub> + nC<sub>2</sub>H<sub>4</sub>, where m + n = 2.

Since the amount of resulting hydrocarbons is not affected by the solvents gasoline, cumene, and a-methyl styrene, the reaction of (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al with CoCl<sub>2</sub> does not pass through radical processes. There are 4 tables.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute of, High-molecular Compounds AS USSR)

SUBMITTED: May 22, 1961

Card 2/2

L 3204-66 EWT(m)/EPF	(c)/EWP(j)/	T RM				
ACCESSION NR: APCOLO AUTHOR: Babitskiy, B Ye. I.; Chesnokova,  TITLE: Stereospecifi plexes	D.; Dogop	VIOV. V. A.44	<i>6</i> 5			
SOURCE: Vysokomoleku TOPIC TAGS: polymeri Abstract: It was sh solutions under the	zation, but	adiene, catal	ysis, macrom	olecular chemi	ne en	
leads to the formati units. The stereos ture of the metal in 50° and the time 8-1 ASSOCIATION: none	and metal h on of a pel ecificity of the Lewis	alides (TiCl <sub>e</sub> ymer with pre of these catal	, VCl <sub>4</sub> , WCl <sub>6</sub> edominantly ( ysts does no	, AlBr <sub>3</sub> , and lup to 94%) club to depend on the	NiCl <sub>2</sub> ) s-1,4- he na-	
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BABITSKIY, B.D.; DOLGOPLOSK, B.A.; KORMER, V.A.; LOBACH, M.I.; TINYAKOVA, Ye.I.; YAKOVLEV, V.A.

Influence of the nature of halogen atom on the stereospecificity of 7-allyl complexes of nickel in butadiene polymerization.

Izv. AN SSSR. Ser. khim. no.8:1507 165. (MIRA 18:9)

l. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S.V. Lebedeva i Institut neftekhimicheskogo sinteza im. A.V. Topchiyeva AN SSSR.

TINYAKOVA, Ye.I.; EYVAZOV, E.Z.

Polymerization of dienes induced by organocalcium compounds. Izv. AN SSSR. Ser. khim. no.8:1508 '65. (MIRA 18:9)

1. Institut neftekhimicheskogo sinteza im. A.V. Topchiyeva AN SSSR.

L 5/011-65 EWT(m)/EPF(c)/EWP(j)/T Pr-4/Pr-4 RM

ACCESSION HR: AP5010579

UR/0020/65/161/003/0583/0585

AUTHORS: Babitskiy, B. D.; Dolgoplosk, B. A. Academician'; Kormer, V. A.; Lobach, M. .. Tinyakova, Ye. ..; Yakoviev, V. A.

TITLE: Stereospecific polymerization of butadiens by catalytic systems based on the M-allyl nickel complexes

SOURCE: AN SSSR. Doklady, v. '6', no. 3, '705, 58\*-585

TOPIC TAGS: polymerization, butadiene, stereospecificity, nickel organic compound,

abstract: The stereospecific catalytic effect of bid- or enoty!) complexes of nickel in the polymerization of butadiene was investigation of butadiene was investigation.

Ni-nations in a ratio of 1:2. It was found that the catalysts cause the formation of 1-4 polybutadiene, consisting mainly (up to 95%) of cis-1,4-rings, and that the more effective catalysts form in the presence of TiOl4. The bis-(N-ally1)-nickel-

bromide catalyst caused the formation of polymers in which the number of cls-rings is equal to that of trans-rings, with the formation of ', 2-rings being negligible. Addition of metal halides to bis- $(\Pi$ -allyl)-nickel-bromide and to bis- $(\Pi$ -crotyl)-

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the entitle of the state of the	All of the polybutadienes f	he catalytic activity and alter ormed contained up to 92% cia-1 lly independent of the nature ormula.	. 4-rings. The structure
Į.	im. 1. 7. Lebedeva All-Uni	auchno-issledovatellakiy instit on Research instructed for Synth in A. 7. Recommendations: ademy of Sciences, SSSR)	etic Subber): Institut
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		OTHER: 003	
Nederland,			
		in fin til til fram mille state fra fram skiller fra fram skiller fram fram fram fram fram skille skiller kli	이 심문에는 어떤 수는 전에 하게 했다. 본 학교 업무에서는 아름이 날아가 되었다. 그는 한 경기는 나는 경기를 받는 모임을 찾아 봤는데 생각이다. 나는
	/,,, Card 2/2		

BAGDASAR'YAN, A.Kh.; FROLOV, V.M.; TINYAKOVA, Ye.I.; DOLGOPLOSK, B.A., akademik

Electric conductivity of alkyllithium solutions in connection with the polymerization process. Dokl. AN SSSR 162 no.6:1293-1296 Je '65.

1. Institut neftekhimicheskogo sinteza im. A.V. Topchiyeva AN SSSR.

APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

TINCGRADOV, F.A.; BOLGGELGSK, B.A., akademih; MGONNIK, V.N.; PARENAGO, C.F.; TINYAKOVA, Ye.L.; TUROV, R.S.

Role of electron-denor additions, water, and alkyhating agents in the store especific polymerization of butsdi ne under the effect of a cobalt catalytic system. Dokl. At SOSR 163 no.501147-1150 Ag 165.

1. Institut neftekhimloheskogo sintaza AN SSSR.

THE REPORT OF THE PROPERTY OF

BABITSKIY, B.D.; DOLGOPLOSK, B.A., akademik; KOMMER, V.A.; LOBACH, M.I.; TINYAKOVA, Ye.I.; YAKOVLEV, V.A.

Stereospecific polymerization of butadiene by catalytic systems based on  $\pi$ -allyl complexes of nickel. Dokl. AN SSSR 161 no.3: 583-585 Mr 165. (MIRA 18:4)

l. Vsesoyuznyy nauchno-issledovatel skiy institut sinteticheskogo kauchuka im. S.V.Lebedeva i Institut neftekhimicheskogo sinteza im. A.V.Topchijeva AN SSSR.

SOV/ 79-28-6-46/63 AUTHORS: Tinyakova, Ye. I., Khrennikova, Ye. K., Dolgoplosk, B. A.

Reactions of Free Radicals in Solution (Reaktsii svobodnykh TITLE: radikalov v rastvore) XIV. The Formation of Free Radicals

in the Decomposition of Hydrogendisulfide and Their Reactions With  $\alpha_m$  and  $\beta$ -Olefines (XIV. Obrazovaniye svobodnykh radikalov pri raspade dvusernistogo vodoroda i ikh reaktsii

s  $\alpha$ - i  $\beta$ -olefinami)

Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1632-1637 PERIODICAL:

(USSR)

The present report deals with the reactivity of the SH radi-ABSTRACT:

cals with  $\alpha$ - and  $\beta$ -olefines; this is of great interest as they play an important part in the sulfur vulcanization process (Ref 4). Hydrogen disulfide was used as source, so to say, of the .SH radicals; the former easily decomposes into HoS and S, which proceeds especially intensely in the presence of alkali liquors and other compounds of basic

character. This decomposition also takes place equimolecular-

Card 1/4 ly in organic solvents, such as xylene, toluene, ethylbenzene

Reactions of Free Radicals in Solution. XIV. The Formation of Free Radicals in the Decemposition of Hydrogendisulfide and Their Reactions With  $\alpha-$  and  $\beta-$  Olefines

etc.; in this connection it must be noted that in the vulcanization of rubber no formation of hydrogen sulfide was observed. Apparently the decomposition of H<sub>2</sub>S<sub>2</sub> takes place according to the chain mechanism through the stage of the •SH- and •S<sub>2</sub>H radicals, as is the case with hydrogen percoxide:

The radical character of this reaction was proved by the decomposition of the hydrogen disulfide in the presence of an acceptor for free radicals, the nitric exide. In the case of a heating in ethylbenzene solution at 70° and a simultaneous passage of gaseous NO no formation of H<sub>2</sub>S<sub>2</sub> takes place. Earlier it was shown that hydrogen sulfide does not enter reaction with NO on the same conditions. The decomposition of hydrogen disulfide in various olefines, containing external and internal double bonds, was investigated. The relative reactivity of the olefines was determined ac-

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Reactions of Free Radicals in Solution. XIV. The Formation of Free Radicals in the Decomposition of Hydrogendisulfide and Their Reactions With  $\alpha-$  and

cording to the composition of the final products and according to the amount of the forming hydrogen sulfide (Tables 1 and 2). In the decomposition of hydrogen disulfide in olefines having a double vinyl bond ( $\alpha$ -pentene, styrene, isoprene) the formation of H<sub>2</sub>S is completely obstructed, which is only partly the case with  $\beta$ -pentene, cyclohexene. The conversion products of H<sub>2</sub>S<sub>2</sub> with  $\alpha$ - and  $\beta$ -pentenes, and cyclohexenes were separated and characterized, and their mechanism of formation were checked. Concluding it may be stated that the reactivity of the  $\alpha$ -olefines with respect to the given radicals is by far higher than that of the  $\beta$ -olefines. There are 1 figure, 2 tables, and 14 references, 10 of which are Soviet.

ASSOCIATION:

Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR i Vsesoyuznyy nauchno-issledovatel'skiy institut sinteti-cheskogo kauchuka

(Institute of High Molecular Compounds, AS USSR and All-Union

Card 3/4 Scientific Research Institute of Synthetic Rubber)

Reactions of Free Radicals in Solution. XIV. The Formation of Free Radicals in the Decomposition of Hydrogendisulfide and Their Reactions With  $\alpha$ - and  $\beta$ -Olefines

SUBMITTED:

September 2, 1957

1. Free radicals--Chemical reactions

Card 4/4

5(3) SOV/20-124-3-29/67

Tinyakova, Ye. I., Dolgoplosk, B. A., Corresponding Member, Academy of Sciences, USSR, Marey, A. I., Al'tshuler, M. Z. AUTHORS:

TITLE: The Production of Crystalline 1-4-Transpolybutadiene and

-Polyisoprene and the Investigation of Their Properties (Polucheniye kristallicheskikh 1-4-trans-polibutadiyena i

poliizoprena i izucheniye ikh gvoystv)

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 3, pp 595-597 PERTODICAL:

(USSR)

ABSTRACT: A description is given of the production of the symmetric

1-4-transpolymers of butadiene and isoprene by the aid of oxide catalysts, in particular of chromium oxides on aluminium silicate. - Polyisoprene is stable, its infrared spec-

trum shows that 99% of the polymer chain possesses the

1-4 trans-configuration. The iodine number corresponds with the theory. Due to the uniform structure, the polymer crystallizes, which could be confirmed by the x-ray photograph. This x-ray photograph is analogous to that of natural β-gutta

percha. - Polybutadiene is a crystalline-fibrous substance.

Card 1/3 As it is difficultly soluble it was pressed into a film

CIA-RDP86-00513R001755810009-5" APPROVED FOR RELEASE: 07/16/2001

SOV/20-124-3-29/67 The Production of Crystalline 1-4-Transpolybutadiene and -Polyisoprene and the Investigation of Their Properties

> prior to the photographing of its infrared spectrum. The spectrum confirms the 1-4 trans-configuration. A curve of the deformation on repeated intensive heating was plotted. A table gives the density changes brought about by heating. The infrared spectrum of polyisoprene was photographed by K. V. Nel'son, and that of polybutadiene by Ye. I. Pokrovskiy, and the x-ray photographs were made by L. A. Volkova. There are 2 figures, 1 table, and 3 references, 1 of which is Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High Molecular Compounds of the Academy of Sciences, USSR)

Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo

kauchuka im. S. V. Lebedeva

(All-Union Research Institute for Synthetic Caoutchouc

imeni S. V. Lebedev)

Card 2/3

5(1) AUTHORS:

Kutsenok, B. Ye., Kulakova, M. N., SOV/20-125-5-53/61

Tinyakova, Ye. I., Dolgoplosk, B. A., Corresponding

Member, AS USSR

TITLE: Initiation of the Polymerization Process in Emulsions

Under the Influence of Isopropyl-benzene-hydroperoxide and SU,

(Initsiirovaniye protsessa polimerizatsii v emul'siyakh pod

vliyaniyem gidroperekisi izopropilbenzola i SO,)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 5,

pp 10/3-10/6 (USSR)

ABSTRACT:

It was proved already earlier (Ref 1) that the reaction between the substances mentioned last in the title proceeds rapidly in hydrocarbon media. It leads to the formation of unsaturated polymers or to the formation of polysuifone if it proceeds in a styrene solution at SO<sub>2</sub> excess (Ref 2).

Therefrom it may be assumed that the reaction of hydroperoxide and  ${\rm SO}_2$  proceeds through an intermediate stage of the free

radicals, in analogy to many other known redox reactions. The

Card 1/4

present paner deals with the investigation of the effective

Initiation of the Polymerization Process in Emulsions 50V/20-125-5-33/61 Under the Influence of Isopropyl-benzene-hydroperoxide and  $50_9$ 

mechanism of this reaction system as woll as with the clarification of its possibility of use for initiating the polymerization of monomers in aqueous emulsions and acid media at low temperature. In vestigation of of the composition of the composition of the interaction products of is opropylable. In vestigation of the interaction process mentioned proceeds instantaneously in an octane-water emulsion between 0 - 70°. SO2 and hydroperoxide are consumed in equimolar quantities (Table 1). If the reaction proceeds in the presence of compensation or competition of the constant of the cons

forms one of the intermediate products of the reaction. The formation of sulfuric acid as a final product of the oxidation may be due to the reaction of the disproportionation of the radicals. If the acceptors of free radicals lack, the reaction proceeds readily in the direction of the formation

Card 2/4

APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

Initiation of the Polymerization Process in Emulsions SOV/20-125-5-33/61 Under the Influence of Isopropyl-benzene-hydroperoxide and SO<sub>2</sub>

of sulfuric acid and carbinol, I n 1 t i a t i c n o f the polymerization under the influence of hydroperoxide SO2. Since the interaction of the components in aqueous emulsions and in a homogeneous medium proceeds rapidly, the first experiments of the afcresaid initiation do not yield positive results. The high concentration of active centers at the beginning of the process caused short reaction chains and the end of polymerization. It is known that such systems may be used for initiating the polymerization only by regulating the rate of interaction of the components by different methods. This is achieved especially at 0° with a gradual dosage of the components. Figure 1 shows the yields of the polymer in the presence of 0.6 % of the hydroperoxide mentioned (computed with respect to the styrene weight) and at an equivalent quantity of 0.1 N SO2-solution according to the sequence of the addition of the components. This shows that with the addition of hydroperoxide and SO2 the polymerization ceases instantaneously

Card 3/4

APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

Initiation of the Polymerization Process in Emulsions SOV/20-125-5-33/61 Under the Influence of Isopropyl-benzene-hydroperoxide and  $SO_2$ 

(at the beginning of the reaction) (Curve 1). The process is quickest at a gradual dosage of the two components. The yield amounts here to 87 % at 0° within 4 hours (Curve 2). Figure 2 shows the kinetic polymerization curves of styrene in the presence of various quantities of hydroperoxide. Above 0.3 % and more of the concentration of the latter the polymerization ceases practically. A complete consumption of hydroperoxide and SO<sub>2</sub> corresponds to this moment. The

polymerization begins again at a temperature rise up to 30° (Fig 3). Therefore an intermediate compound is produced under certain conditions which is able to initiate the polymerization at higher temperatures. There are 3 figures, 2 tables, and 8 references, 4 of which are Soviet.

ASSOCIATION:

Nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S. V. Lebedeva (Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev)

SUBMITTED: Card 4/4

January 5, 1959

18(5)
5(1)

S/019/59/000/22/218/439
1003/D002

AUTHORS:

Yevdokimov, V.F., Dolgoplosk, B.A., Poddubnyy, I.Ya., Tinyakova,
Ye.I. and Aver'yanov, S.V.

TITLE:

A Method of Mammfacturing Titanium Trichloride, Lower Titanium Chlorides and Metallic Titanium

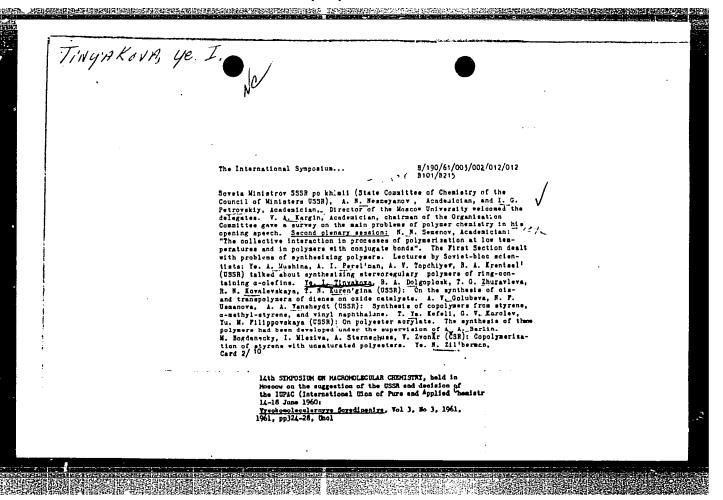
FERIODICAL:

Byulleten' izobreteniy, 1959, Nr 22, p 53 (USSR)

ABSTRACT:

Class 40a, 4650. Nr 124123 (619889/22 of 18 February 1959). No description is given.

Card 1/1



850円 S/062/60/000/02/08/012 B003/B066

5.3200 AUTHORS:

Dolgoplosk, B. A., Yerusalimskiy, B. L., Kuren'gina, T. N.,

Tinyakova, Ye. I.

TITLE:

Reactions of Free Radicals in Solutions. 15th Report. Destruction Mechanism of Polymers by Free Radicals

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,

1960, No. 2, pp. 311 - 316

TEXT: The authors investigated the destruction of polyisobutylene dissolved in ethyl benzene under the action of disulfides, benzoyl peroxide, isopropyl benzene-hydroperoxide, triazenes, dimethyl-diphenyl-tetrazene, iron- and cobalt naphthenate. The destructive effect of the individual agents may be seen from the diagrams in Figs. 1, 2, and 3. The following conclusions may be drawn from the investigations and pertinent papers by other authors: The destructive effect is most intense in such free radicals as are especially active in the reaction of H-separation. The destruction takes place in such a manner that first a H-atom is separated from the polymer chain and, secondly, the C-C bonds of the polymer radical

Card 1/2

Reactions of Free Radicals in Solutions. S/062/60/000/02/08/012 15th Report. Destruction Mechanism of Polymers B003/B066 by Free Radicals

thus formed are spontaneously freed. The authors mention a paper by L. M. Romanov (Ref. 2). There are 3 figures and 14 references: 8 Soviet, 4 American and British, and 2 German.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk

SSSR (Institute of High-molecular Compounds of the Academy

of Sciences USSR)

SUBMITTED: June 19, 1958

N

Card 2/2

APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

DOLGOPLOSK, B. A., YERUSALIMSKIY, B. L., KROPUCHEVA, Ye. N., TINYAKOVA, Ye. L.

"Structure of Diene Polymers as a Function of the Nature of Catalytic Systems"

Report presented at the Conference on International Symposium on Macromolecular Chemistry. Montreal, Canada, 27 July to 1 August 61.

"Institute for Higher Moecular Compounds, Akademia Nauk, SSSR, Leningrad, USSR.

APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

S/020/62/146/004/013/015 B117/B186

AUTHORS:

Dolgoplosk, B. A., Corresponding Member AS USSR, Tinyakova,

Yo. ...

TITLE:

Mechanism of the action of complex catalysts during polymeriza-

tion

PERIODICAL:

Akademiya nauk SSSR. Doklady, v. 146, no. 4, 1962, 856-859

TEXT: Here the usual assumption that polymerization in the presence of mixed catalysts (such as those of Ziegler, Natta, etc.), is chiefly characterized by a coordination-anion system is challenged. From a number of well-known reactions it can be shown that the cation mechanism too may prevail in polymerization of many systems, which contradicts the concept of chain growth via the C-Al bond. The effectiveness of the cation mechanism is corroborated by: (1) the ability of some mixed catalysts to initiate cis-trans-isomerism in unsaturated polymers and the polymerization of isobutylene, vinyl ether, and  $\beta$ -butene; (2) the positive action of water, HCl, AlCl, and alkyl halides on the polymerization of some compounds. According to a scheme developed by G. Natta (J. Inorg. and Card 1/3

Mechanism of the action of ...

S/020/62/146/004/013/015 B117/B186

Nucl. Chem., 8, 86, 1960; Tetrahedron, 8, 8 (1960)) fragments of the initial organo-aluminum compound are assumed to remain at one of the ends of the polymer chain, which do not directly participate in the chain growing process but which might be connected with the active centers. This scheme may help to explain the incorporation of organo-aluminum compounds into the polymer chain and the possible development of a cation type polymerization process when an anion type C - Al bond is present. This is an indication of possible participation of organo-aluminum compounds in the chain rupture. It is shown that, when the chain breaks as a result of interaction between the active "cation" end and the inactive "anion" end, annular polymer molecules may sometimes form. In this case, the active center regenerates. The possibility of such a reaction is revealed by the polymerization of butadiene with  $TiCl_4 - R_2AlCl$ , whereby a cyclic trimer is obtained in an almost quantitative yield. This may be taken as proof that the two carbon ends of the chain are oppositely charged. It is noted that the statement made above does not exclude the anion type of some coordination systems, for example, organo-aluminum compounds and alkoxy compounds of titanium and molybdenum. The polymerization of these compounds presumably takes place via the  $Card \cdot 2/3$ 

Mechanism of the action of ...

S/020/62/146/004/013/015 B117/B186

δ-**δ**+

C-Me bond.

ASSOCIATION:

Institut khimicheskoy fiziki Akademii nauk SSSR (Institute

of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED:

June 9, 1961

Card 3/3

15,9201

S/020/62/146/002/008/013 B101/B144

AUTHORS:

Dolgoplosk, B. A., Corresponding Member AS USSR,

Tinyakova, Ye. I.

TITLE:

Polymerization mechanism of dienes and the structure of

the polymer chain

PERIODICAL:

Akademiya nauk SSSR. Doklady, v. 146, no. 2, 1962, 362-365

TEXT: The effect produced on the structure of the resulting polymer by the following configurations of the monomer link at the growing chain end during the polymerization of butadiene and its 2-derivatives is discussed on the basis of previous publications (see below):

Polymerization mechanism of ...

S/02C/62/146/CC2/CC5/C:3 B101/B144

For radical and cation mechanisms, the configurations (3) or (6) assumed, for polymerization by alkali alkyls, the configurations (2) or (5). Free ions do not form when combined catalysts of the Ziegler type are used. The formation of 1,4-trans links follows a cationic coordination mechanism (A)  $\binom{-1}{+}$ , and that of 1,2 links follows an anionic coordination The former is suited for the polymerization and cationic monomers such as vinyl alkyl ethers and isobutylene, the latter for the polymerization of anionic monomers such as vinyl cyanide, vinyl chloride, etc. In the presence of anionic active centers, it is unlikely that the growing chain end reacts with double bonds in the chain itself to form cyclic side groups. Cis-trans isomerization of the links takes place in radical mechanisms, especially in the cationic mechanism of initiatier. In anionic mechanisms it may occur under the action of a cation belonging to the organometallic compound of the catalyst complex. The investigation of these problems in Ziegler-type anionic coordination systems is important. The most important English-language references are: J. Maynard, W. Mochel, J. Polym. Sci., 13, 251 (1954); J. Kuntz, A. Card 2/3

\$/020/62/146/002/008/013 Polymerization mechanism of ... B101/B144

Gerber, J. Polym. Sci., 42, 299 (1960); A. V. Tobolsky, C. E. Rogers, J. Polym. Sci., 40, 73 (1959); T. S. Lee, I. M. Kolthoff, M. A. Mairs, J. Polym. Sci., 3, 66 (1948).

Institut khimicheskoy fiziki Akademii nauk SSSR (Institute-ASSOCIATION: of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED: June 9, 1962

(ard 3/3

APPROVED FOR RELEASE: 07/16/2001 CIA-RDP86-00513R001755810009-5"

38280 5/190/62/004/006/006/026 B101/3110

5.3830

AUTHORS:

Tinyakova, Ye. I., Dolgoplosk, B. A., Kuren gina, T. N.

TITLE:

Polymerization under the action of catalytic systems containing cobalt or tungsten carbonyls and diethyl

aluminum halide

PERIODICAL:

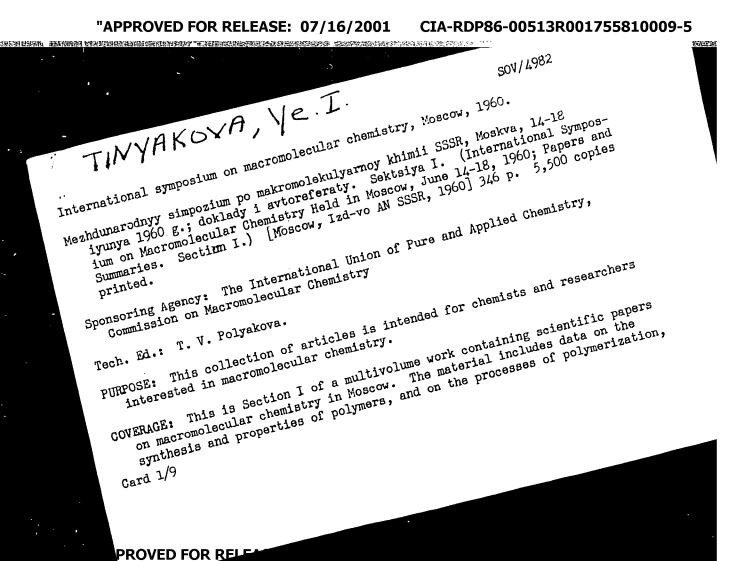
Vysokomolekulyarnyye soyedineniya, v. 4, no. 6, 1962,

828-834

TEXT: The authors investigated the catalytic effect of the precipitate formed when  $Co(CO)_4$  or  $V(CO)_6$  dissolved in hydrocarbons are mixed with  $\text{Al}(\text{C}_{2}\text{H}_{5})_{2}\text{Cl.}$  The following were polymerized with the cobalt complex (ratio carbonyl: R<sub>2</sub>AlCl = 1:5): isoprene (20°C, 2.5 hr, polymer yield 31%), butadiene (50°C, 1.5 hr, yield 25%; 2.5 hr, yield 40%), styrene (20°C, 3 hr, 29.8%), α-methyl styrene (80°C, 42 hr, 47.2%), and α-butene (50°C, 48 hr, 7%). The investigation of the structure of butadiene polymerized with the cobalt or tungsten complexes gave the following results irrespectively of the temperature (40-50°C) and of the ratio Card 1/2

S/190/62/004/006/006/026 B101/B110 Polymerization under the ... carbonyl :  $R_2$ AlCl (1 : 2.5 to 1 : 16): 65-87% cis-1,4 bonds, 5-8% trans-1,4 bonds, and 5-7,6 1,2 bonds. Isoprene polymerized with the cobalt complex (20-50°C) contained 61-62% cis-1,4 bonds, 22-23% trans-1,4 bonds, and 14-16% 3,4 bonds. An analysis of the precipitate formed from  $Co(CO)_4$  and  $Al(C_2H_5)_2Cl$  showed: ratio Co: Al between 1: 1.25 and 1: 3; ratic Al : Cl $\sim$ 1 : 1; ratio CO : Co $\sim$ 1; ratio C<sub>2</sub>H<sub>5</sub> : Al $\sim$ 1 : 1. Since no gases are released during the formation of the precipitate, a reaction of CO with  ${
m Al}({
m C}_2{
m H}_5)_2{
m Cl}$  is assumed, similar to that occurring with organolithium and organomagnesium compounds. The absorption of CC by  $Al(c_2H_5)_2Cl$ and the formation of sec-amyl alcohol were proved experimentally. OAl(R)Cl CoCO · AlR2Cl · R2CC is suggested for the catalytic complex. There are 1 figure and 3 tables. Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute ASSOCIATION: of High-molecular Compounds AS USSR) SUBMITTED: April 1, 1961 Card 2/2

# "APPROVED FOR RELEASE: 07/16/2001



International Symposium (Cont.) SOV/4982 copolymerization, polycondensation, and polyrecombination. Each text is presented in full or summarized in French, English, and Russian. There are 47 papers, 28 of which were presented by Soviet, Rumanian, Hungarian, and Czechoslovakian scientists. No personalities are mentioned. References TABLE OF CONTENTS: Pino, P., G. P. Lorenzi, and L. Lardicci (Italy). Isotactic Polymers of Goldenberg, N., and R. Istratoiu (Rumania). Influence of Synthesis Conditions on Some Physicochemical Properties of Polypropylene Tinyakova, Ye. I., B. A. Dolgoplosk, T. G. Zhuravleva, R. N. Kovalevskaya, and T. N. Kuren'gina (USSR). The Synthesis of Cis- and Trans-Diene Polymers on Oxide Catalysts and a Study of Their Structure and Properties Butler, K., P. R. Thomas, and G. J. Tyler (Great Britain). Stereospecific 13 Polymerization of Some Polar Vinyl Monomers Card 2/9 21

TINYAKOVA, Ye.I.; DOLGOPLOSK, B.A.; VYDRINA, T.K.; ALFEROV, A.V.

Cation activity of the components in a "cobalt" system and the nature of the end groups in a polymeric chain. Dokl. AN SSSR 152 no.6:1376-1378 0 '63. (MIRA 16:11)

1. Institut neftekhimicheskogo sinteza AN SSSR. 2. Chlen-korrespondent AN SSSR (for Dolgoplosk).

DOLGOPLOSK, B.A.; TINYAKOVA, Ye.I.

Certain regularities in the process of ionic polymerization. Dokl. AN SSSR 154 no.4:857-860 F '64. (MIRA 17:3)

1. Institut neftekhimicheskogo sinteza AN SSSR. 2. Chlen-korrespondent AN SSSR (for Dolgoplosk).

ACCESSION NR: AP4012970

8/0020/64/154/004/0857/0860

AUTHORS: Dolgoplosk, B.A. (Corresponding member); Tinyakova, Ye. I.

TITLE: Certain principles of the ionic polymerization process

SOURCE: AN SSSR. Doklady\*, v. 154, no. 4, 1964, 857-860

TOPIC TAGS: ionic polymerization, cationic polymerization, coordination ionic polymerization, radical polymerization, polymerization rate, polymerization inhibition, isobutylene propylene system, 2,3-diene polymerization, conjugated diene olefin system, cyclopentadiene inhibition polymerization

ABSTRACT: The relationship that the reactivity of the monomer increases with decreasing reactivity of the radical and the rate of homopolymerization or chain growth is discussed. It is applicable to ionic and coordination-ionic systems as well as to radical polymerization. Various examples are cited to support the conclusion that small amounts of a more active monomer have an inhibiting

Card 1/2

ACCESSION NR: AP4012970

effect on the cationic polymerization process: small amounts of isobutylene or vinylalkylethers inhibit polymerization of less active monomers such as propylene, butadiene, or styrene; 2,3-dimethylbutadiene retards polymerization of butadiene; ethylene "regulates" the stereospecific polymerization of butadiene in a Co catalyzed system, lowering the molecular weight of the polybutatiene; in mixtures of conjugated dienes with ethylene or  $\alpha$ -olefins, the more active diene retards polymerization of the olefin; in the dienes and of cyclopentadienes, addition of a small amount (0.01%) of cyclopentadiene inhibits polymerization of butadiene. Orig. art.

ASSOCIATION: Institut neftekhimicheskogo sinteza, Akademii nauk SSSR (Institute of Petrochemical Synthesis, Academy of Sciences

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OTHER: 005

Card 2/2

DOLGOPLOSK, B.A., akademik; BABITSKTY, B.D.; KORMER, V.A.; LOBACH, M.I.; "INYAKOVA, Ye.I.

Link formation mechanism in the stereospecific polymerization of dienes. Dokl. AN SSSR 164 no.6:1300-1302 0 165.

(MIRA 18:10)

1. Institut neftekhimicheskogo sinteza AN SSSR i Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S.V.Lebedeva.

EWT(m)/EPF(c)/EWP(j)/T L 2634-65 ACCESSION NR: AP5023367 AUTHORS: Sharayev. O. Tinyakova, Ye. I.; (Academician) TITLE: Transition from metal hydrides to  $\overline{M}$ -allyl complexes and the initiation of the stereospecific polymerization of butadiene 144,65 SOURCE: AN SSSR. Doklady, v. 164, no. 1, 1965, 119-121 TOPIC TAGS: polymer, catalysis, metal hydride, polymerization, stereospecificity, butadiene ABSTRACT: The reaction of nickel hydrides with butadiene was investigated. It was found that nickel hydrides initiate the cis-polymerization (90%) of butadiene through a stage of M-crotyl complex formation. In other reactions the nickel amount passing to benzene solution was 20% of that calculated for unreacted ethyl magnesium bromide. The gaseous products evolved during the decomposition of the crotyl derivatives of nickel were mixtures of butenes (with a predominant amount of <-butene). The total yield of butenes was more than 1 mole per mole of organomickel compound. The stereospecific polymerization of butadiene with the formation of 1,4-polymer was investigated using nickel on kieselguhr and Raney **Card** 1/2

L 2684-66

ACCESSION NR: AP5023367

nickel as catalysts (at 32-42C, for 3 hours) and using benzene and heptane as solvents (at 45% by volume butadiene concentration) in the presence of TiCl<sub>4</sub>, VCl<sub>4</sub>, AlC<sub>3</sub>. The tabulated data show that the nature of the metal in the Lewis acid does not affect the microstructure of the polymer chain. The polymerization is effective in both benzene and heptane. Considering the data of nickel transition reacted with butadiene to M-crotyl derivatives, it can be assumed that analogous reactions occur on the surface of nickel catalysts. Orig. art. has: 1 table.

ASSOCIATION: Institut neftekhimicheskogo sinteza im. A. V. Topchiyeva, Akademii nauk SSSR (Institute of Petrochemical Synthesis, Academy of Sciences, SSSR)

SUBMITTED: 27Mar65

ENCL: 00

SUB CODE: GC, OC

NO REF SOV: 004

OTHER: 008

Card 2/2

L 52264-65 EPF(c)/EMP(j)/EWT(m)/T Pc-4/Pr-4 ESD ACCESSION NR: AP5010832 UR/0020/65/161/004/0836/0838 AUTHOR: Babitskiy, B. D.; Golenko, T. G.; Kormer, V. A.; Skoblikova, V. I.; Tiryakova, Ye. I.; Dolgoplosk, B. A. (Academician) TITLE: Stereospecific polymerization of butadiene in the presence of catalyst systems based on w-cyclopentadienyl complexes of nickel 7 SOURCE: AN SSSR. Doklady, v. 161, no. 4, 1965, 836-838 TOPIC TAGS: stereospecific polymerization, polymerization, butadiene polymerization, butadiene, pi-complex ABSTRACT: Polymerization of dienes was studied with catalyst systems composed of m-cyclopetadienyl Ni-complexes and Lewis acids. These systems represent a new group of stereospecific polymerization catalysts as they do not contain compounds with a o-metal-hydrocarbon bond. Benzene solutions of bis-m-cyclopentadienyl Ni-complex and appropriately in-reveled as tendent Ni-complexes along with metal palidom are ette ti**ve** catalyet of roles, election of distance. . Solar of the production of the production of the solar of t ib ab angon sime chees incluymentality a experiodents were last Card 1/3

L 52264-65

ACCESSION NR: AP5010832

the test duration was 17 hours. Butadiene concentration in the total solution was 2.5 mol/L and concentration of metal halides was  $5 \times 10^{-3}$  mol/L. Polymers were precipitated with HCl acidified ethyl alcohol. The yield and molecular weight of the polymers is a function of the type of Lewis acid used and the ratio between individual components of the datalyst system. A (m-C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Mi-TiCl<sub>4</sub> datalyst system yielded a polymer containing about 90% cis-1,4 groups, 5 to 10% trans-1,4 groups, and ro side vinyl groups. Highest polymer yields were obtained with a Mi:Ti ratio of 1. The polymer molecular weight was not higher than 100,000. The  $(\pi-C_2H_5)_2Ni$ -VCl4 catalyst system yields polybutadiene containing up to 96% cis-1,4 groups. Maximum catalytic activity results from a Mi:V ratio of 1, the molecular weight of the polymer is 400,000 to 500,000. The catalyst based on tin-, molybdenum-, and tungsten halides yield polymers with 20 to 50% trans-1,4 groups. Depending upon reaction conditions, (π-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ni-AlX<sub>3</sub> catalysts (where X is Cl or Br) yield polybutadiene of 20,000 to 50,000 molecular weight. Catalysts based on π-cyclopeta--dienyl-π-cyclopentenyl Ni-complexes perform similarly to bis-π-cyclopentadienyl based systems; both yield polybutadiene containing 92-95% cis-1,4 groups. "The authors are highly indebted to I. G. Kolokoltseva for synthesis of the bis-m--cyclopentadienyl Ni-complex." Orig. art. has: 2 tables.

Card 2/3

L 52264-65		
ACCESSION NR: AP5010832		···
Kauchuka im. S. V. Lebedava	nauchno-issledovatelskiy ins a (All-Soviet Institute of S akademii nauk SSSR (Institu	titut sinteticheskogo ynthetic Rubber); Institut te Setrochemical Synthesis,
SUBMITTED: 21Dec64	ENCL: 00	SUB CODE: GC, MT
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<u>64482-65</u> - ENT(m)/EPF(c)/ENP(j)/T/ENF(t)/ENF(b) —IJP(c)— JD/HY人。 ACCESSION NR: AP5021280 UR/0020/65/163/005/1147/1150 AUTHORS: Vinogradov, P. A.; Dolgoplosk, B. A. (Academician); Zgonnik, V. N.; O. P.; Tinyakova, Ye. I.; Turov, B. S. TITLE: The role of electron-donor additives, water, and alkylating agents in the stereospecific polymerization of butadiene under the influence of a cobalt catalytic system SOURCE: AN SSSR. Doklady, v. 163, no. 5, 1965, 1147-1150 TOPIC TAGS: stereospecific polymerization, polymer, butadiene, cobalt, catalyst ABSTRACT: The object of the investigation was to enlarge the currently available information concerning the stereospecific catalytic activity of cobalt catalytic systems (B. S. Turov and P. A. Vinogradov i dr., DAN, 155, 874, 1965). The polymer studied was butadiene. The experimental results are shown graphically in Figs. 1 and 2 on the Enclosure. It is concluded that the addition of AlCla, RAIC12, Br2, H20, CH2 = CH - CH2 halogen, RC1 - Al - O - Al - RC1 increases the formation of 1,4 cis rings, the molecular weight, and the rate of polymerization, whereas the addition of R<sub>3</sub>Al, RSR, ROR, R<sub>3</sub>N, KCl, and NaCl decreases the number Card 1/4

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of 1,2 rings, the molecular weight, and the rate of polymerization. Orig. art. has: 1 table, 3 graphs, and 3 equations.

ASSOCIATION: Institut neftekhmicheskogo sinteza, Akademii nauk SSSR (Institute for Potrochemical Synthesis, Academy of Sciences SSSR)

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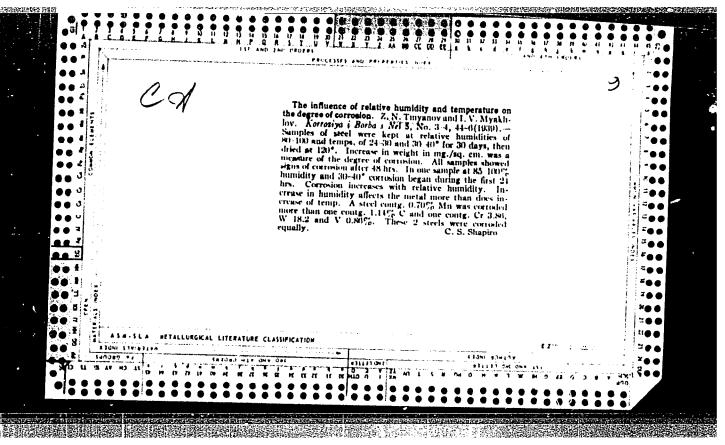
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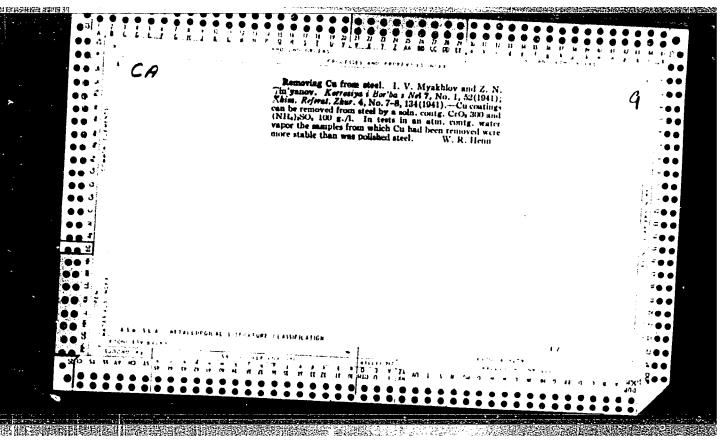
ACC NR: AP6030022 ( ) SOURCE CODE: UR/0020/66/169/005/1102/1103 AUTHOR: Oreshkin, I. A.; Chernenko, G. M.; Tinyakova, Ye. I.; Dolgoplosk, B. A. (Academician) ORG: Institute of Petrochemical Synthesis im. A. V. Topcheviy, Academy of Sciences SSSR (Institut neftekhimicheskogo sinteza Akademii nauk SSSR) TITLE: π-allyl derivatives of chromium and titanium as catalysts for steoreospecific polymerization of butadiene SOURCE: AN SSSR. Doklady, v. 169, no. 5, 1966, 1102-1103 TOPIC TAGS: chromium, titanium, polymerization catalyst, polybutadiene ABSTRACT: Stereospecific polymerization of butadiene was studied at 20-80°C using 2.7 mol/l concentration of butadiene in toluene and 0.2 mol/% (based on butadiene) of chromium and titanium triscrotylates as catalysts. The polymerization duration was 2-68 hr. In some experiments the catalysts were supplemented with NiCl<sub>2</sub> (MR<sub>3</sub>:NiCl<sub>2</sub>= = from 1:8 to 1:24) with  $TiJ_4(MR_3:TiJ_4=1:1)$ , or with  $O_2(Mr_3:O_2=1:0.5)$ . The chromium system was prepared by reacting anhydrous CrCl; with crotylmagnesiumchloride in an ether toluene mixture (1:2 by volume) at -10° to -20°C. The titanium system was prepared by reacting anhydrous TiCl3 with biscrotyl magnesium in diethyl ether solvent at -5°C; the ratios of TiCl; to R-Mg was from 5:1 to 12:1. The polymer yields varied from 6.1 UDC: 542.952+541.64 Card 1/2

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nate of ( nas:	was 1 2 or 7 2 Ta	found to hter/lum bles:	result oxide,	in a po	polymer with polymer showed	or $(C_4H_7)_3Ti$ $I_4$ to either $I_4$ $85-93\%$ of $I_4$ $I_4$ $I_4$ $I_5$ $I_7$ $I_$	chromium I-cis uni 1,3-tran	or titanium t ts. In the p s units. Ori	riscroto- resence g. art.
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Effect of saline components of the medium on the amylase, catalase and peroxidase activity of Bac. subtilis and Bac. mesentericus.

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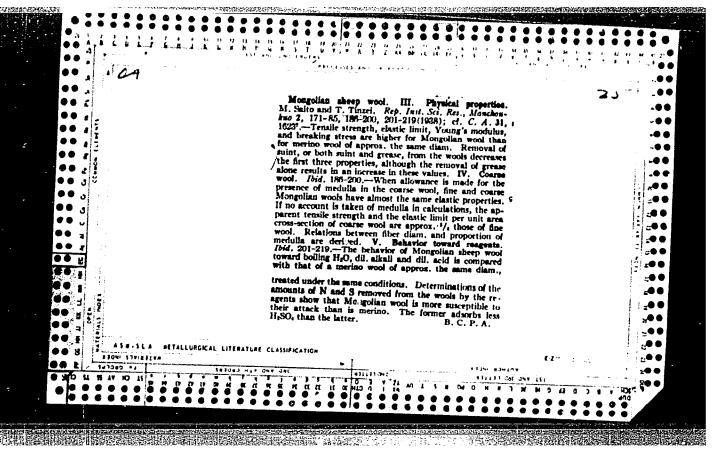
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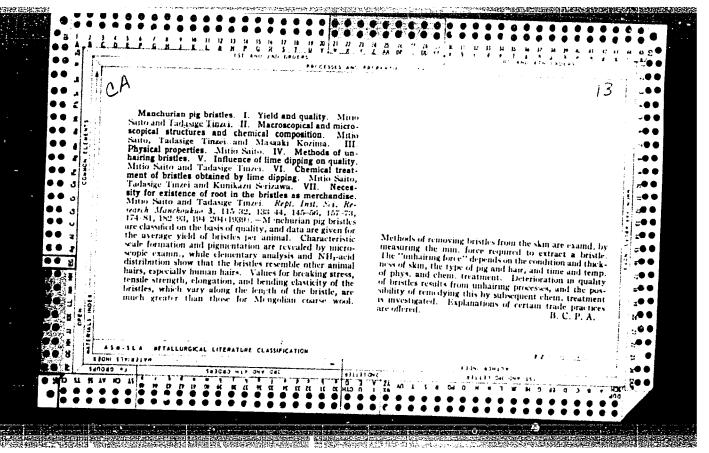
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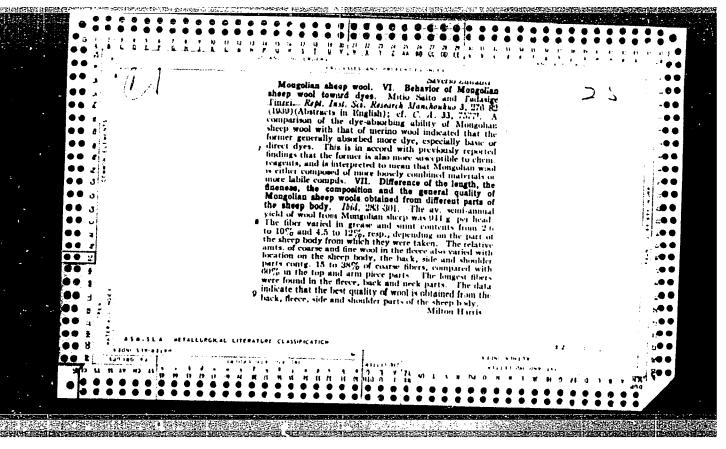


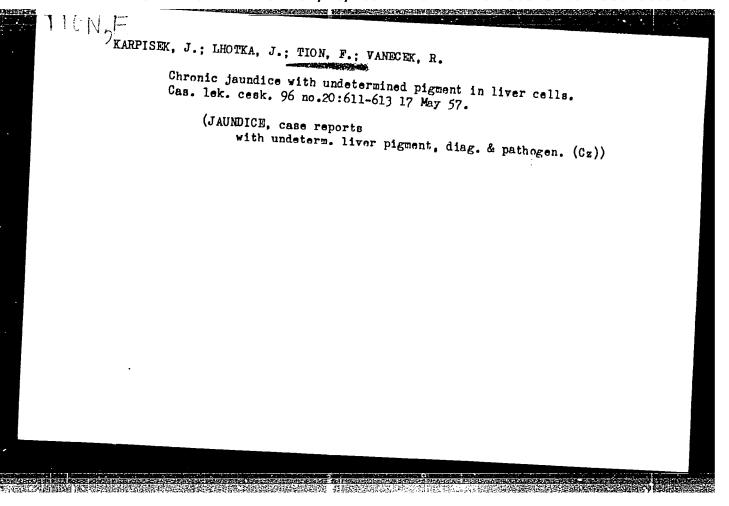
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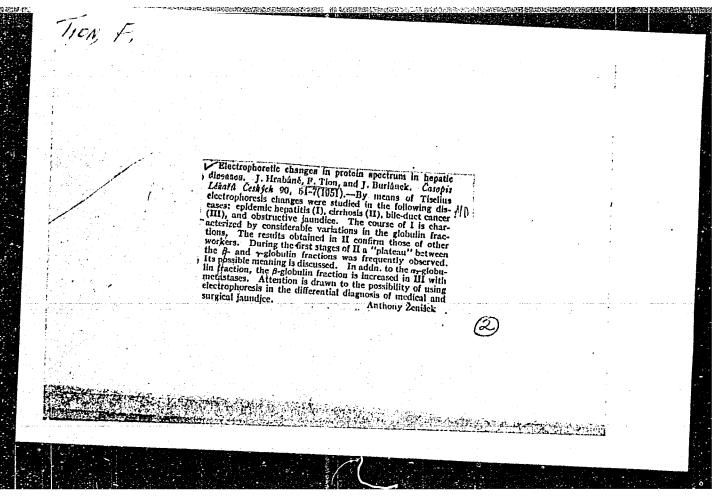
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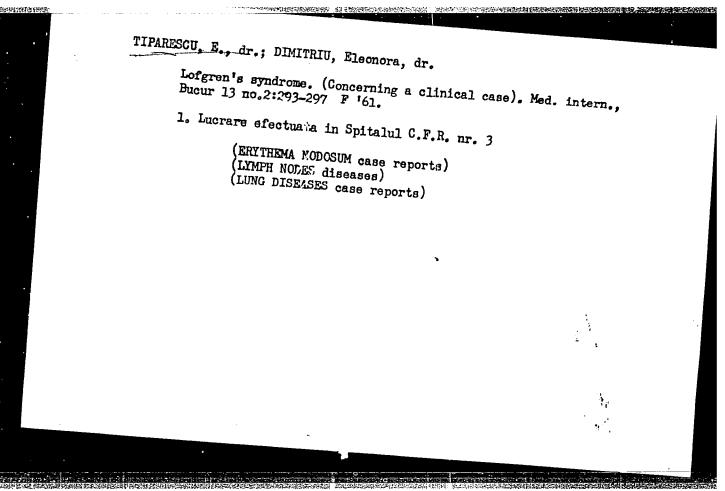
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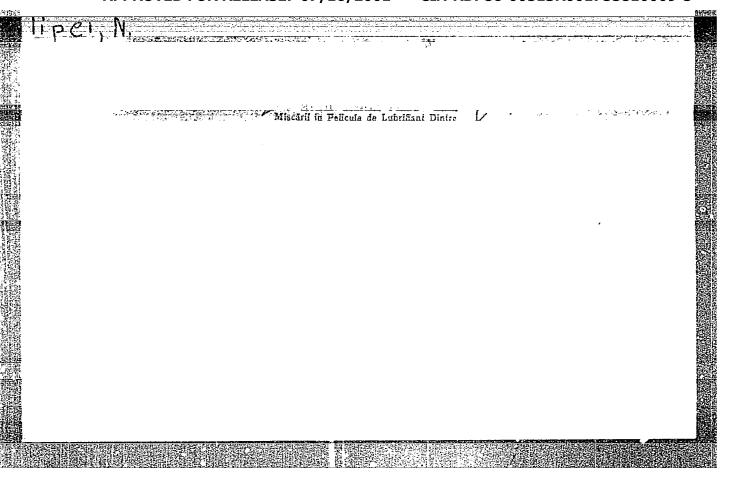
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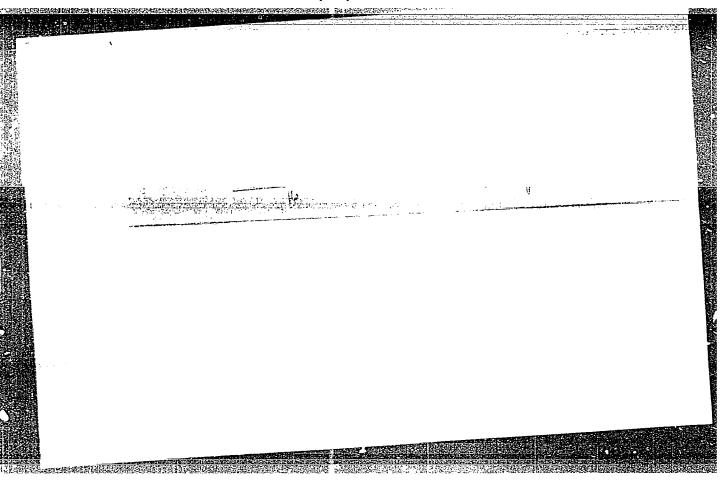


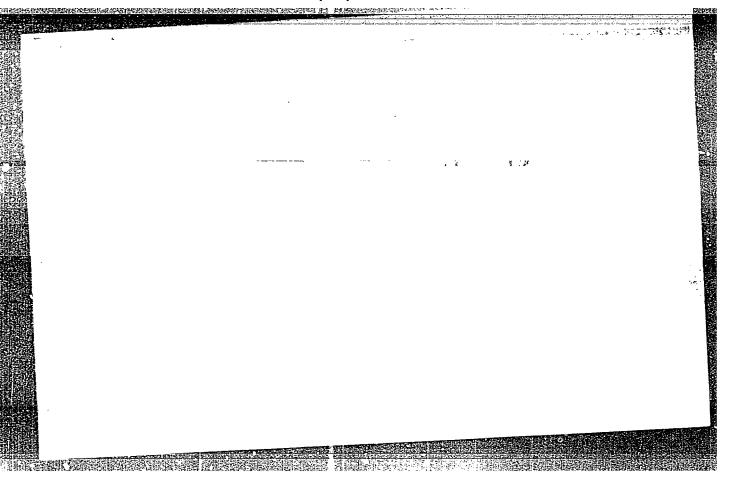
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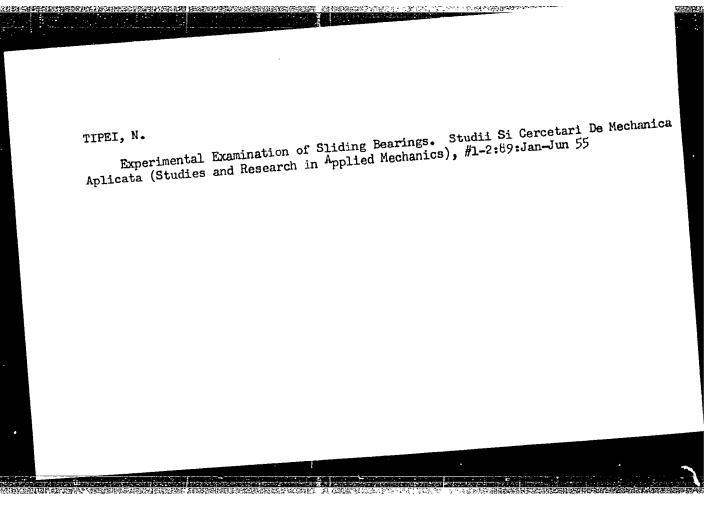
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